

Phthalate Ester Plasticizers—Why and How They Are Used

by P. R. Graham*

Introduction

Phthalate esters have been found in the environment. They have also been detected in humans and animals. We do not know how they enter the environment nor do we know if they present a hazard to mankind. Strong evidence exists pointing to the natural occurrence of the phthalate moiety. However, we do not know to what extent these natural sources contribute to the total amount found in the environment.

This meeting of industrial, academic, medical, and government scientists from many disciplines will give the public, whom we all serve, a better understanding of these issues than if we individually pursued our separate courses. The public deserves the best scientific opinions we can give them — opinions based on meaningful research and interpreted with unemotional perspective.

The objective of this presentation is to provide specific aspects of plasticizer technology and market data necessary for environmentalists and toxicologists to understand the possible points of entry of these phthalate esters into the environment or the human body: the esterification process; ester transport; polymer-plasticizer process; end-uses; disposal; natural sources.

Only a small portion of the storehouse of plasticizer technology can be reported here. Phthalates are used in virtually every major

product category (construction, automotive, household products, apparel, toys, packaging, and medical products) resulting in high market fragmentation. Therefore, these market data are our best estimates.

History

Modern plasticizer technology, although rooted in the art of primitive people in their search for materials based on natural products, is now based on a broad spectrum of scientific principles utilizing a vast array of synthetic and naturally occurring compounds (1). The first commercially significant plasticizers were discovered shortly after the development of cellulose nitrate in 1846. Castor oil was patented for this use in 1856 (2). In 1870 camphor became the plasticizer of choice for cellulose nitrate (3). Celluloid remained the major thermoplastic material until shortly before World War II.

The introduction of phthalate esters in the 1920's overcame the excessive volatility and undesirable odor of camphor. However, the commercial availability of poly(vinyl chloride) in 1931 and the synthesis of di-2-ethylhexyl phthalate in 1933 quickly shifted emphasis away from cellulose nitrate and started the rapid growth of the flexible poly(vinyl chloride) industry (4). Today, this industry comprises thirteen major suppliers of phthalate plasticizers. Approximately 1 billion pounds of some 20 different phthalate compounds (Fig. 1) will be manufactured in 1972 (5). In addition, ca. 350,000,000 lb. of

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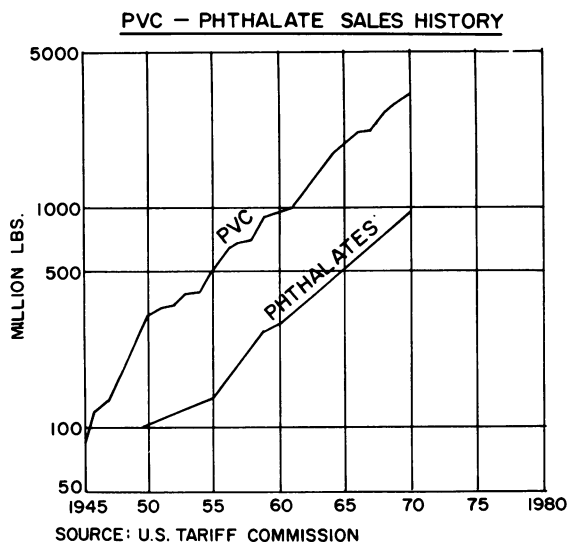


FIGURE 1. Poly(vinyl chloride) and phthalate sales history.

other plasticizer types are used for special purposes such as high permanence, flame retardance and low-temperature performance. These include adipates, azelates, phosphates, epoxides, polyesters, and trimellitates.

Some Theoretical Aspects of Plasticization

Plasticizers are interfused with high polymers to increase flexibility, extensibility, and workability. This is achieved by lowering the glass transition temperature to below room temperature. The polymer is changed from a hard glasslike solid to a flexible, tough elastomer. Poly(vinyl chloride) is unique in its acceptance of plasticizers. Its polarity, helical structure, and balance of amorphous and crystalline regions in its molecular geometry provide compatibility for a large number of plasticizer structures over relatively wide concentration and temperature ranges. Interestingly, the addition of minor concentrations of plasticizers to poly(vinyl chloride) actually makes the system more rigid. This phenomenon is called "antiplasticization." Using x-ray diffraction, Horsley (6) has shown that these embrittled systems are more ordered (crystalline) due to the increased freedom of motion when a low concentration of plasticizer is present. Higher

levels of plasticizer redissolve these crystallites and effect plasticization.

Compatibility

The first consideration in the selection of the optimum plasticizer for any use is its compatibility with the polymer. Incompatibility can result in either an obvious, unsightly phase separation (exudation, crystallization) or more subtly, loss of long-term permanence.

Among many theories of plasticizer compatibility, the following are most frequently used to predict or to measure compatibility of plasticizers with poly(vinyl chloride) and other resins.

Flory-Huggins Interaction Parameter—In this theory (7), the polymer-diluent interaction parameter χ is calculated from the equation:

$$\frac{1}{T_m} = \frac{1}{T_m^0} + \frac{RV_u}{\Delta H_u V_1} (U_1 - \chi U_1^2)$$

where T_m is the depressed melting temperature; T_m^0 is the melting temperature of pure polymer; V_u and V_1 are molar volumes of the polymer unit and diluent, respectively; R is the gas constant; ΔH_u is the heat of fusion per mole of polymer units; U_1 is the volume fraction of diluent; and χ is the polymer-diluent interaction parameter. According to the theory, χ must be 0.5 or lower for the polymer-diluent pair to be compatible. The phthalate esters, particularly di-2-ethylhexyl phthalate, satisfy this criterion. Maximum compatibility is obtained between dibutyl phthalate and di-2-ethylhexyl phthalate. The χ value for each of these esters is -0.05 .

Solubility parameter—The cohesive-energy density (CED) measures the strength of intermolecular interactions in a pure liquid or solid. The solubility parameter δ is obtained from the equation (8):

$$\delta^2 = \frac{\Delta E}{V} = \frac{(\Delta H_v - RT)}{V} = \text{CED}$$

where E is the molar energy of vaporization; H_v is the heat of vaporization (per mole); V is the molecular volume; R is the gas constant; and T is the (absolute) temperature. The use of the solubility parameter to predict plasticizer compatibility assumes that same overall intermolecular interactions are present in the plasticizer as well as the polymer. This empirical method does not distinguish between types of attractive forces between organic molecules such as dipole-dipole, dipole-induced-dipole, or hydrogen bonding. The solubility parameter in conjunction with the dielectric constant provides an excellent prediction of plasticizer compatibility (9). Phthalate plasticizers have solubility parameters between about 8.4 and 11.4 and dielectric constants between about 4 and 9. Poly(vinyl chloride) has a calculated solubility parameter of ca. 9.6 by the method of Small (10).

Permanence

If a plasticized poly(vinyl chloride) surface is placed in contact with other materials, the plasticizer may migrate or extract from the polymer matrix. When the environment (air, oil, water, blood, etc.) has a very high affinity for the plasticizer, the migration rate is dependent upon the ability of the plasticizer to diffuse through the resin matrix to the attracting media. This is matrix controlling (11):

$$Q/S = 2.26 (Dt/L^2)^{1/2}$$

where Q is the weight (grams) of plasticizer lost in t hours; S denotes total weight (grams) of plasticizer in film; D is the diffusion constant (cm/hr); and L is film thickness (cm). The diffusion constant depends upon the plasticizer molecular weight, modulus of the system, the compatibility of plasticizer, plasticizer viscosity, and the affinity of environment for the plasticizer.

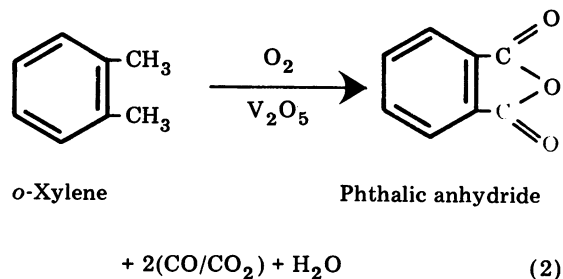
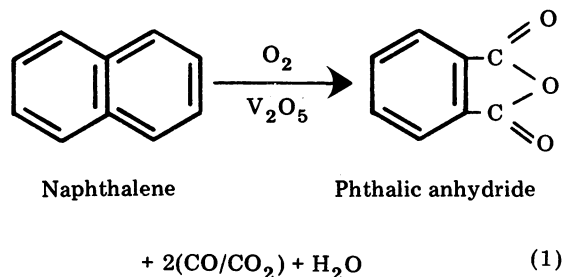
When the resistance to loss from the surface is high compared to the resistance of the sheet itself, the migration is controlled by the surface resistance and is proportional to the first power of the thickness. This is

the case when the environment has little affinity for the plasticizer such as air. Migration rate is directly dependent upon temperature in both cases. The higher the temperature, the higher the rate of extraction or migration.

Plasticizer Technology

Chemistry

Phthalate esters are prepared from phthalic anhydride and the appropriate alcohol. Equations (1) and (2) show typical commercial processes for phthalic anhydride from either naphthalene or *o*-xylene as basic raw materials. Phthalic anhydride from modern processes assays above 99.5%. The remaining 0.5% could be phthalic acid, isophthalic acid, terephthalic acid, and maleic anhydride.



99.5% Phthalic acid
 0.5% { Isophthalic acid
 Terephthalic acid
 Maleic anhydride

The alcohols are manufactured by two basic processes: The Ald-Ox process and the Oxo process (12). 2-Ethylhexanol is produced from the Ald-Ox process using propylene as the starting material to form C_4 aldehyde. An aldol condensation produces C_8 aldehyde, which is hydrogenated to 2-ethylhexanol. Butyl alcohol is also made as a byproduct in this process. The Oxo process is used to produce both essentially linear and branched chain alcohols from olefins. The olefin is reacted with CO and H_2 to form an aldehyde which is then hydrogenated to an alcohol. Linear alcohols are made from linear olefins produced by the Ziegler process starting with ethylene. Branched chain alcohols are prepared from branched olefins which occur in refinery operation. Both the Ald-Ox and the Oxo processes are typified in Figure 2.

The esterification process is shown in eq. (3). The purity of esters from modern esterification processes range from 99.70% to 99.97%.

Polymer-Plasticizer Process

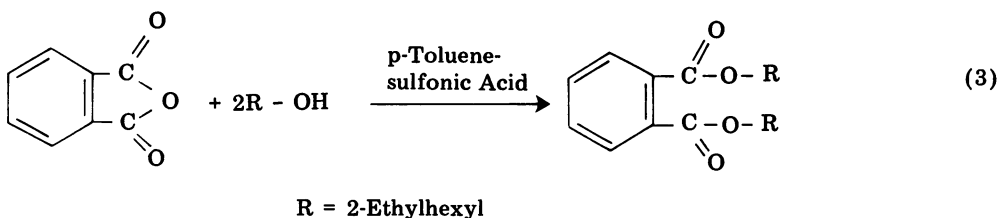
In almost all applications of flexible poly(vinyl chloride), heat must be employed to obtain the necessary degree of fusion between the plasticizer and the resin (13). Figure 3 shows three typified processing routes commonly employed in the manufacture of flexible poly(vinyl chloride).

A wire insulation compound would follow route at the top of Figure 3. The resin, plasticizer, stabilizer, and filler would first be mixed in a ribbon or high-intensity blender. The temperature of the blend could increase to 50–75°C; however, the compound is not fused at this point but rather emerges as a free-flowing powder. The powder is usually masticated on a hot-roll mill at

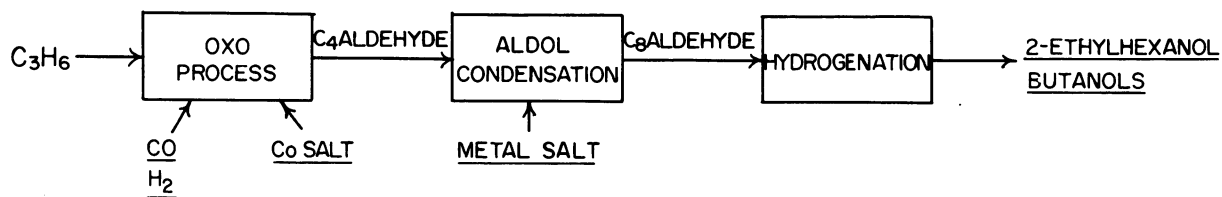
150–160°C and formed into a fused sheet. The sheet is pelletized and forced through a hot extruder to form the insulation around the metal wire. The ribbon blender, high-intensity mixer, and the extruder are closed systems. Roll milling is an open process but is generally equipped with an exhaust system.

Flexible poly(vinyl chloride) film is also usually prepared from the route at the top of Figure 3. If it is extruded, the process is quite similar to that described for wire insulation. Poly(vinyl chloride) film is often calendered. When this process is used, the dry blend is masticated in a closed Banbury mixer at 150–160°C. The calendering process forms the uniform film. It operates at fusion temperatures and is an open, but usually exhausted process. Incineration of the vapors is sometimes employed.

An example of the process shown on the bottom of Figure 3 is the manufacture of leatherlike fabric for upholstery. A special type of poly(vinyl chloride) is dispersed in the plasticizer using a rotary mixer. This dispersion, called a plastisol, is cast on a web of fabric by using a knife or a roller coater. Both of these operations are performed at room temperature. The plastisol-coated fabric is passed through an oven where it fuses at temperatures ranging from 160 to 180°C. Modern ovens are equipped with exhaust systems to vent the volatilized vapor which in some instances is incinerated. Certain poly(vinyl chloride) copolymers can be dissolved in solvents containing phthalate and other plasticizers to form lacquers and other solution coatings. These coatings are applied by spray or brush; the solvent is evaporated providing functional surfaces for a number of substrates. Very little heat, if any, is required for fusion. This process is also depicted in Figure 3.



I ALD - OX PROCESS



II OXO PROCESS

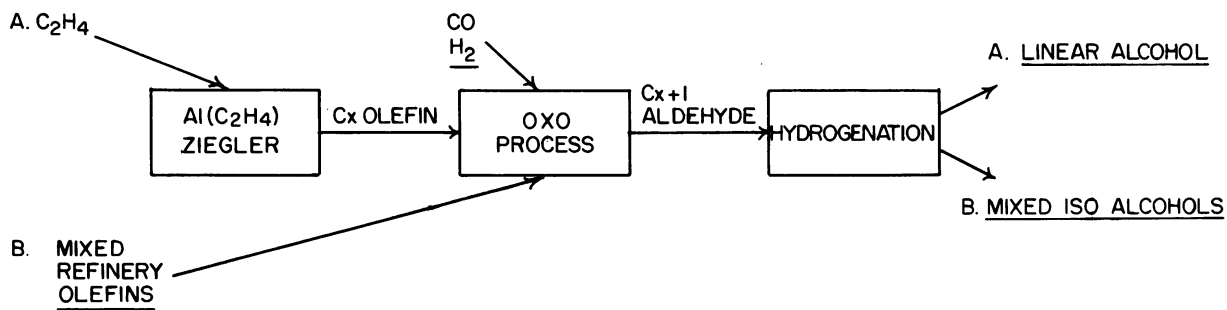


FIGURE 2. Ald-Ox and Oxo processes.

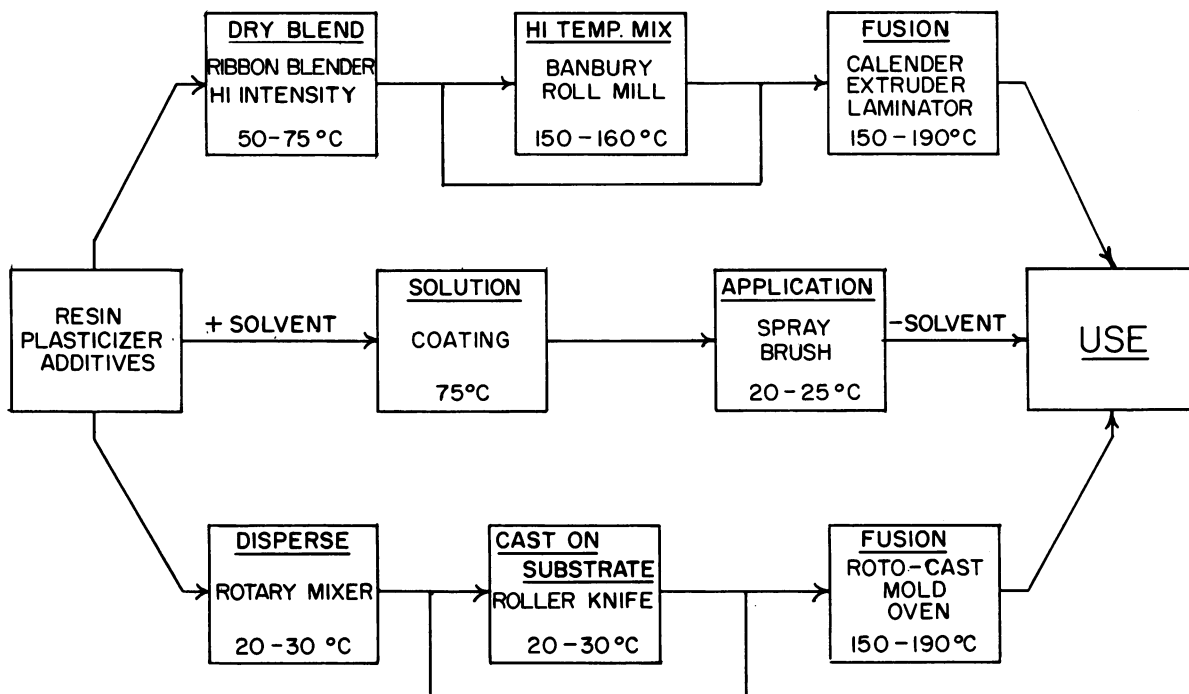


FIGURE 3. Processing of plasticized poly(vinyl chloride).

Plasticizer Uses and Markets

No single plasticizer exhibits the perfect balance of properties for every application. Each end-use will demand certain essential properties. To achieve this balance some properties of lower importance must be sacrificed to some extent. In the judicious selection of the "proper" plasticizer system for a given application, the first consideration would be compatibility. Then, depending upon the specific application, other criteria relating to processing, performance, and permanence properties would be obtained. A partial checklist might be as shown in Table 1.

Table 1. Criteria relating to processing, performance, and permanence properties.

Processing	Performance	Permanence
Roll milling	Toxicity	Migration resistance
Calendering	Color	Volatility
Dry blending	Odor	Extraction resistance
Banburying	Flexibility	Outdoor aging
Extrusion	Softness	Light stability
Solution	Mechanical properties	Heat sensitivity
Foaming	Electrical properties	Fungal resistance
Heat sealing	Flame retardance	

It should also be remembered that for each application the desirable balance of properties must be achieved within a prescribed cost framework.

Table 2 lists selected performance criteria for a number of plasticizer types, including both branched-chain and linear phthalates. The results from the permanence property evaluations were obtained by using standard accelerated testing procedures. These data compare classes of products and are not meant to characterize individual plasticizers within these classes. The measurement for each property (H_2O extraction, volatility, oil resistance, and migration) is expressed in terms of per cent weight loss. Therefore, the higher the number, the poorer the performance. The low-temperature efficiency value is the temperature at which the modulus of rigidity is 135,000 psi, making those systems with the lowest values the most efficient in flexibilizing poly(vinyl chloride) at low temperatures. The room temperature modulus is the flexibility of the system at room temperature. Again, the lower the modulus, the better the performance is.

The adipates, being linear aliphatic esters, are used primarily for their plasticizing efficiency. They flexibilize poly(vinyl chloride) well at both room temperature and extremely low temperature. This efficiency is obtained at the expense of permanence. The aliphatic structure leads to poor hydrocarbon resistance, and the relatively low molecular weight causes high volatility. The

Table 2. Performance criteria for selection of plasticizers.^a

	Permanence properties,				Efficiency	
	H_2O , %	Volatility, %	Oil, %	Migration %	Low temp, °C	R.T. modulus, psi
Adipate	0.10	14	70	21	-66	630
Phthalate (branched)	0.03	5	34	4	-39	830
Phthalate (linear)	0.02	2	44	2	-48	850
Phosphate ester	0.02	7	7	9	-39	700
Trimellitate	0.01	1	82	2	-42	850
Polymeric ester	0.10	2	2	0.4	-20	1300

^a 40% plasticizer in PVC.

adipates are used in food wrap film, garden hose, and other applications where low-temperature performance is needed.

The phthalate esters give a good overall balance of properties. They are not as flexibilizing as the adipates, but are more permanent. They can, however, have poor hydrocarbon or fat resistance. This probably explains the presence of DEHP in blood after storage in poly(vinyl chloride) bags. The linear phthalates, except for hydrocarbon resistance, are more efficient than DEHP or other branched chain phthalates. As a class, the phthalates are the most widely used plasticizers. DEHP is regulated by the FDA for use in the packaging or storing of high water content food.

The trimellitate plasticizer is just becoming a commercially important system because of its extremely low volatility and high aqueous media resistance. The high degree of aliphaticity results in very poor oil and fat resistance. The trimellitates are used in wire insulation and certain automotive uses where high-temperature performance is required.

The phosphates are used generally to provide flame retardance.

The polyester polymeric plasticizer is a reasonable alternate to phthalates for certain critical applications where a high degree of permanence is required. A polyester plasticizer based on butylene glycol, adipic acid, and a natural fatty acid (Santicizer 334F) was introduced for these critical uses in

1971. The high molecular weight of this polyester (MW = 2000) provides the excellent permanence in both hydrocarbon and aqueous environments. This polyester is regulated under FDA 121.2511 (Plasticizers for Polymeric Substances).

The volatile loss of plasticizer during use is an important consideration in the study of possible environmental hazards. Table 3 exhibits data from an accelerated test designed to compare several plasticizers in their tendencies to volatilize from a flexible poly(vinyl chloride) surface such as upholstery. A stream of air was blown over a film 10 mil thick and having an exposed surface of 240 cm². The film contained 70 phr (parts per hundred parts of resin) plasticizer. The temperature was maintained at 83°C (185°F). The flow rate was 250 cm³/min. These results indicate that the linear alkyl phthalate ester is a vast improvement over DEHP. Further improvement can be achieved through the use of diundecyl phthalate or trialkyl trimellitate.

An analysis of the atmosphere inside a new automobile disclosed a concentration of organic material to be ca. 12 µg/l. Over 60 different organic compounds were detected. The phthalate portion of this organic mixture was found to range from 0 to 6%, depending upon temperature conditions. At the lower temperatures, the phthalates were undetectable. Some of the other organic materials found were: C₂–C₅ alkylbenzenes, C₉–C₁₈ alkanes, higher alkanes, naphthalene, phenol, and di-*tert*-butyl cresol.

The automobile studied was new. It was driven approximately 2000 miles, during which time no smoking, dining, or storage of materials was permitted.

Plasticizer Markets

The major market categories accounting for over 90% of the plasticizer uses of phthalate esters are listed in Table 4. Tables 5–9 provide further breakdown in each of these major market classifications (14).

There are several known nonplasticizer uses of phthalate esters. These are shown in

Table 3. Plasticizer volatility from vinyl film at 83°C.^a

Plasticizer	Plasticizer volatility	
	µg/l. of air	µg/hr
Di-2-ethylhexyl phthalate	3.4	51
	2.3	36
	2.5	39
	3.3	49
	2.9	44
Linear phthalate (trialkyl, C ₇ , C ₉ , C ₁₁)	0.75	11.3
	0.65	9.9
	0.70	10.6
Diundecyl phthalate	≤0.005	≤ 0.22
Trialkyl trimellitate	<0.0009	< 0.04

^aMeasured in a circular flow cell, 240 cm² film area, 70 plasticizer, flow rate 250 cm³/min.

Table 4. Plasticizer uses of phthalate esters.

Use	Phthalate usage, lb x 10 ⁻⁶
Building and construction	387
Home furnishings	203
Transportation	114
Apparel	72
Food surfaces and medical products	46
Total	1022

Table 5. Building and construction.

Use	Phthalate usage, lb x 10 ⁻⁶
Wire and cable	185
Flooring	150
Swimming pool liners	20
Weatherstripping	13
Window splines	10
Other	9
Total	387

Table 6. Home furnishings.

Use	Phthalate usage, lb x 10 ⁻⁶
Furniture upholstery	90
Wall coverings	38
Housewares	30
Garden hose	15
Appliances	10
Other	20
Total	203

Table 7. Transportation.

Use	Phthalate usage, lb x 10 ⁻⁶
Upholstery and seatcovers	80
Auto mats	15
Auto tops	12
Other	10
Total	114

Table 8. Apparel.

Use	Phthalate usage, lb x 10 ⁻⁶
Footwear	45
Outerware	20
Baby pants	7
Total	72

Table 9. Food surfaces and medical products.

Use	Phthalate usage, lb x 10 ⁻⁶
Food wrap film	18
Closures	7
Medical tubing	15
Intravenous bags	6
Total	46

Table 10. Nonplasticizer phthalate uses.

Pesticide carriers
Cosmetics
Fragrances
Munitions
Industrial oils
Insect repellent

Total sales: estimated 50 x 10⁶ lb

Table 10. The total sales volume is a rough estimate of 50 x 10⁶ lb in 1972. These numbers are not generally reported making it difficult to pinpoint how much phthalates are used in each area. Since the esters are not bound by a resin matrix, as in plasticization, it would appear that some of these uses would provide a direct route into the environment.

Biodegradation of Phthalates

The laboratory data in Table 11 compare the biodegradability of DEHP and butyl benzyl phthalate with a biodegradable deter-

gent, linear alkylbenzene sulfonate. The results were obtained by using a semicontinuous activated sludge at a feeding rate of 5 mg/48 hr.

Natural Occurrence of Phthalate Moiety

A recent literature search (15) has revealed a number of possible natural sources of the phthalate moiety (Table 12).

Some questions relating to possible phthalate contamination from the equipment and instruments employed in these analyses have arisen. However, several of these procedures were carefully reviewed to assure the absence of poly(vinyl chloride) tubing or other artificial sources of phthalate ester. It is interesting that Paul Karrer's textbook (16) was published prior to the emergence of flexible poly(vinyl chloride) as a major commercial plastic material.

Table 11. Laboratory biodegradability study. ^a

	Amount disappearing in 48 hr, %	Refractory residue
Linear alkylbenzene sulfonate	99+	None
Di-2-ethylhexyl phthalate	91	None
Butyl benzyl phthalate	99	None

^aSemicontinuous activated sludge at 5 mg/48 hr.

Table 12. Naturally occurring phthalates reported in the literature.

Source	Type of phthalate	Reference
Vegetation		
Poppies	Phthalic acid	(16, 17)
Cranberries		(18)
Eucalyptus oil	Phthalate, mp 200°C	(19)
Olive oil ^a		(20)
Japanese Canadences	DMP, DIAP, DHP, DOP	(21)
Cigar smoke	Phthalic	(22)
Tobacco leaves	Phthalate esters, trimellitates	(23)

Source	Type of phthalate	Reference
Grapes	DBP	(24)
Kewda	Phthalate ester	(25)
Oxidized corn oil	DOP	(26, 27)
Animal		
Atolla jellyfish	Phthalic acid	(28)
Humans ^b	DOP	(29)
Bovine heart, pineal gland	DOP	(30)
Milk ^c		(31)
Fish meal lipids ^d		(32)
Fungus		(33)
Mineral		
Soil		(34)
Crude oil		(35)
Shale		(36)

^a 1.2-6.4 ppm in 16 samples, Naples, Italy.

^b Source probably artificial.

^c Source probably tubing.

^d Could be artifact.

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